

## Band Structure and Fermi Surface of Electron-Doped C<sub>60</sub> Monolayers

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C<sub>60</sub> fullerides are challenging systems because both the electron-phonon and electron-electron interactions are large on the energy scale of the expected narrow band width. We report angle-resolved photoemission data on the band dispersion for an alkali-doped C<sub>60</sub> monolayer and a detailed comparison with theory. Compared to the maximum bare theoretical band width of 170 meV, the observed 100-meV dispersion is within the range of renormalization by electron-phonon coupling. This dispersion is only a fraction of the integrated peak width, revealing the importance of many-body effects. Additionally, measurements on the Fermi surface indicate the robustness of the Luttinger theorem even for materials with strong interactions.

Exhibiting properties such as high transition temperature superconductivity (1) and anti-ferromagnetism (2), C<sub>60</sub>-based fullerides are

ideal model compounds for exploring key conceptual issues in strongly correlated physics (3). As in typical molecular systems, the

bands formed through the overlap of the C<sub>60</sub> molecular levels are expected to be narrow, on the order of 0.5 eV for the lowest unoccupied molecular orbital (LUMO)-derived band (4). On the other hand, the Coulomb repulsion between electrons is larger [more than 1 eV (5)], and some phonons have very high energies [up to 200 meV (3)] comparable to the expected bandwidth of half-filling. This set of parameters suggests a totally non-conventional behavior: On one hand, the strong electron-electron interaction predicts the proximity of metal-insulator transitions of the Mott-Hubbard type, whereas the high phonon frequencies predict a breakdown of the adiabatic approximation. In angle-integrated photoemission measurements (AIPES), the width of the LUMO peak, which naively corresponds to the band width, appears much wider (~1 eV) than the theo-

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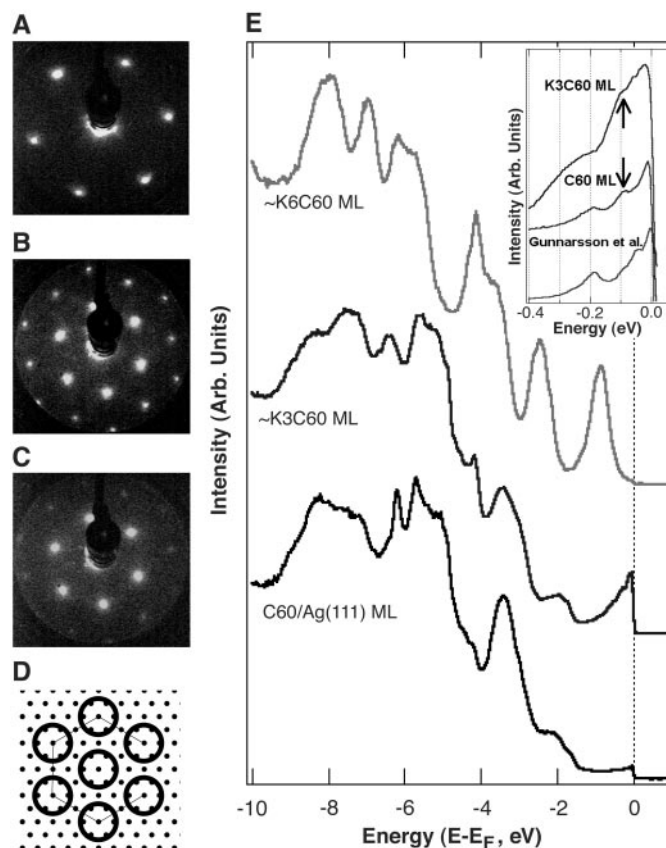
retical estimation. Although of fundamental importance to addressing this issue, the observation of band dispersion has remained elusive after a decade of intense efforts. This is a testimony to the technical challenges imposed by the detection of such a narrow band, with threefold degeneracy, in a small Brillouin zone (BZ), as well as particular matrix element effects and/or disorder in samples. We detected with synchrotron light a clear band dispersion of 100 meV for a  $C_{60}$  monolayer doped by K to approximately half-filling, indicating that the width of the AIPES measurement is mainly because of many-body effects. The experimental results are compared with a theoretical calculation performed for the same monolayer system. Both the band width and Fermi velocity are renormalized by 40 to 50% as compared with the maximum bare theoretical dispersion of 170 meV and the calculated Fermi velocity. This upper bound of renormalization is within the range explainable by electron-phonon coupling alone using values of the electron-phonon coupling constant from the literature (3). This suggests that the electron-electron correlation is not substantial in reducing the bandwidth in our monolayers although it is expected to be strong in this system (3, 5). An extremely short mean-free path can be inferred from the momentum peak width but does not preclude a complete mapping of the Fermi surface (FS). Its volume obeys the Luttinger theorem, although the complex interactions and short mean-free path may question its validity.

We carried out high-resolution angle-resolved photoelectron spectroscopy (ARPES) on single crystalline K-doped  $C_{60}$  monolayers prepared in situ. The ARPES data presented here were collected with photon energy of 35 eV and with the direction of incident beam polarization almost perpendicular to the sample surface, whereas results have been confirmed with the use of other photon energies and on different samples (6).

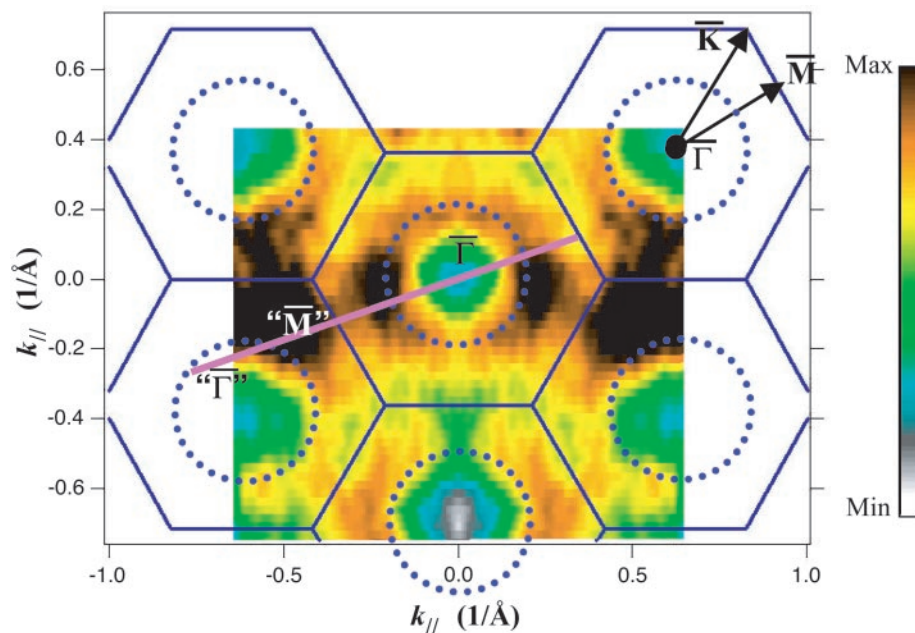
A thick multilayer  $C_{60}$  film, grown at 400 K, was annealed at above 600 K to yield a  $C_{60}$  monolayer (7–9). K was then introduced

with the use of an SAES getter source [for example, (7, 10)]. The low-energy electron diffraction (LEED) patterns (Fig. 1, A to C)

indicate a hexagonal lattice structure of  $C_{60}$  monolayer (Fig. 1, B and C) on the Ag(111) surface (Fig. 1A). The distance between  $C_{60}$



**Fig. 1.** LEED patterns and angle-integrated photoemission data. LEED patterns of (A) a clean Ag(111) surface at 114 eV electron beam energy, (B) a pure  $C_{60}$  monolayer at 22 eV, and (C) a  $K_3C_{60}$  monolayer at 22 eV. The orientation of the hexagon in (B) and (C) is rotated by  $30^\circ$  compared to (A). (D) Schematic view of the real space structure of  $C_{60}$  molecules (larger circles) on Ag(111) surfaces (small dots). (E) Valence band measured by angle-integrated photoemission on  $C_{60}$ ,  $K_3C_{60}$ , and  $K_6C_{60}$  monolayers (MLs). The inset is an enlargement of the spectra near Fermi level as compared to data digitized from (12).



**Fig. 2.** Integrated spectral weight near the Fermi energy on  $K_3C_{60}$  monolayer. BZ boundaries (straight lines) are calculated on the basis of LEED. Dotted circles are guides showing a ring-like shape surrounding each  $\Gamma$  point. The occupied states are along zone boundaries. The data were taken in the left half of the color image and were symmetrized along the  $x = 0$  line accordingly with symmetry consideration. The purple line shows the measuring direction for the dispersion in Fig. 3.  $k_{||}$  is the electron momentum, and the color scale indicates the minimum and maximum of the intensity.

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molecules is estimated to be 10.02 Å from the Ag fcc lattice constant (Fig. 1D).

Figure 1E depicts three AIPES data measured on  $C_{60}$  films with and without K doping. For the pure  $C_{60}$  monolayer, there is a small contribution to the density of states at the Fermi level because of the charge transfer from the Ag substrate. With K doping, the LUMO-derived band, which is triply degenerated (4), is filled by electrons from K up to  $K_6C_{60}$  (7, 11). By integrating the LUMO peaks in AIPES data and taking the  $K_6C_{60}$  spectra as a reference with charge transfer of 6 (Fig. 1E), we estimated the charge transfer to  $C_{60}$  molecules to be about 0.7 for the pure  $C_{60}$  monolayer [comparable to 0.75 in (7)], and 3.3 for the intermediately K-doped sample, which we refer to as a  $K_3C_{60}$  monolayer hereafter. The peak at the Fermi level, together with the shoulders at higher energy (Fig. 1E, inset), resemble those observed in the gas-phase  $C_{60}^-$ , where the shoulders were interpreted in terms of phonon satellites (12, 13). This feature is clearer in the pure  $C_{60}$  monolayer compared to K-doped samples. The 100-meV phonon behavior is enhanced compared with the gas-phase data, suggesting

a modification due to band structure effect and/or electron-phonon coupling.

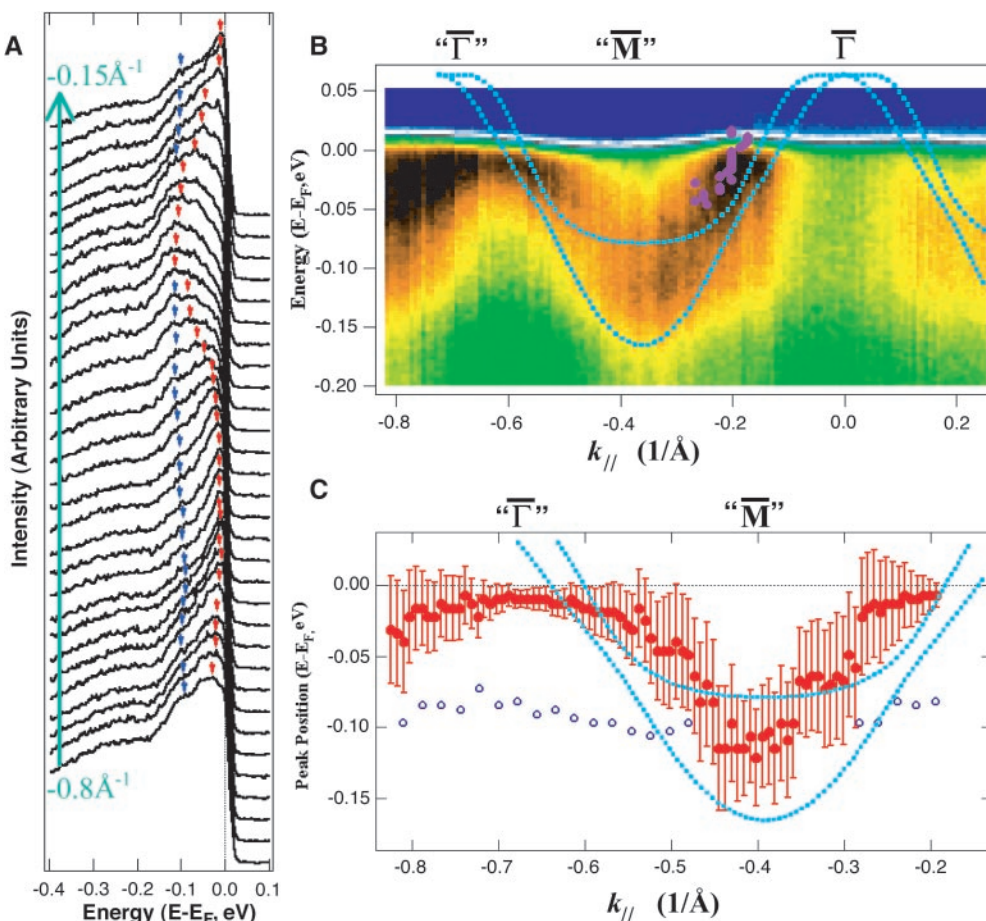
The two-dimensional (2D) FS map of the  $K_3C_{60}$  monolayer (Fig. 2) shows a periodicity in momentum space that matches very well with the  $C_{60}$  BZ deduced from LEED. This map, obtained by integrating the spectral weight over a  $\pm 20$ -meV energy window at the Fermi level throughout the BZ, shows a ring encircling low spectral intensity around each  $\bar{\Gamma}$  point for all the BZs. As discussed below, these low-intensity regions are unoccupied states, so we have a hole-like circular 2D FS around each  $\bar{\Gamma}$ . The change of the intensity at the equivalent symmetric points may be because of matrix element effect and/or asymmetries from measuring geometry. A similar result was also verified with the use of 45-eV photons.

The dispersion of the partially filled conduction (LUMO-derived) band was determined, approximately along the  $\bar{\Gamma}$ - $\bar{M}$  direction (purple line in Fig. 2), from angle-resolved EDCs (energy distribution curves). The band disperses in the energy scale of about 100 meV and crosses the Fermi level at 0.15 to 0.2 Å<sup>-1</sup> in momentum space (Fig. 3, A to C). This result shows

that the closed area around the  $\bar{\Gamma}$  point is “unoccupied,” and the occupied states are along the BZ boundary, complementing the results of the FS map (Fig. 2). To extract the shape of the dispersion quantitatively near the Fermi level, we studied the MDCs (momentum distribution curves), and the positions of the MDC peaks around Fermi level are shown as the purple dots in Fig. 3B. The Fermi velocity,  $v_F$ , defined as the slope of the dispersion at Fermi energy ( $E_F$ ), is  $7.9 (\pm 0.9) \times 10^6$  cm s<sup>-1</sup>, corresponding to an effective mass of  $m^*$  equal to  $2m_e$  to  $4m_e$  ( $m_e$  is the free electron mass).

For quantitative analysis, we studied the crystal and electronic structures of  $K_3C_{60}$  monolayers with the use of ab initio pseudopotential density functional calculations (14–17) in the local density approximation (LDA). The positions of the three K atoms and the center of mass of the  $C_{60}$  molecule are relaxed according to ab initio forces on top of the Ag surface represented by six layers of Ag atoms. The calculated LUMO-derived band dispersions are so sensitive to the orientations of  $C_{60}$  molecules that we can determine a very specific orientation of  $C_{60}$  as a model for the experimental samples by comparing the theoretical disper-

**Fig. 3.** Band dispersion measured on a  $K_3C_{60}$  monolayer at 35 eV photon energy. The measuring direction, which is approximately along  $\bar{\Gamma}$ - $\bar{M}$ , is indicated by the purple line in Fig. 2. (A) Angle-resolved EDCs with emission angle from  $-0.8$  Å<sup>-1</sup> ( $-16.5^\circ$ ) to  $-0.15$  Å<sup>-1</sup> ( $-3^\circ$ ). The red arrows show the main peak position, also plotted in (C) as the red solid circles, corresponding to the band dispersion. The weak peak at 100 meV (blue arrows), also shown as the blue circle in (C), is probably because of phonon shake-up structure. (B) Image plot of photoelectron intensity versus energy and emission angle. Data were collected on two samples below and above  $x = -0.2$  Å<sup>-1</sup>, respectively, with very good reproducibility. Color legend is the same as that of Fig. 2. The band disperses above Fermi level around each  $\bar{\Gamma}$  point. For comparison, two subbands from theoretical calculations are shown as dotted lines. At the second BZ, the intensity below Fermi level around “ $\bar{\Gamma}$ ” is probably because of the misalignment (about  $12^\circ$  off the  $\bar{\Gamma}$ - $\bar{M}$  direction as shown in Fig. 2), which may also mix some contribution of the  $\bar{\Gamma}$ - $\bar{\Gamma}$  component. This misalignment also contributes to the a-little-shorter experimental  $\bar{\Gamma}$ -“ $\bar{\Gamma}$ ” distance as compared to theory. The extremely narrow band and small BZ make high zone measurements more difficult. (C) The maximum peak position of EDCs in (A) (red solid circles). The error bars correspond to the peak widths in (A). The dotted lines are again the calculated bands, which are shifted left by  $0.03$  Å<sup>-1</sup> ( $0.6^\circ$  in emission angle, within experimental error bar) to match the experimental data better. We cannot resolve the two subbands in our experiments, but the maximum experimen-



tal dispersion (100 meV) is smaller than that of the theoretical one (170 meV). This gives an upper bound of renormalization, although it can be smaller if one takes some sort of average of the theoretical bands.



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sions with the experiments. The obtained model orientation (Fig. 4A), whose total energy is only 0.1 eV per  $C_{60}$  higher than the minimum, is very close to that in solid  $K_3C_{60}$ . Because the energy difference is so small ( $\sim 1 \times 10^{-3}$  rydberg per atom), it is well within the uncertainties of the LDA for van der Waals solids.

The calculated LUMO-derived bands (Fig. 4B) are not occupied around the  $\bar{\Gamma}$  point, consistent with experimental data (Fig. 3B). The maximum width of the occupied band is 170 meV, and the Fermi velocities are  $1.2 \times 10^7$  and  $1.6 \times 10^7$  cm s $^{-1}$  for two LUMO-derived subbands, respectively. Both the band width and the Fermi velocity overestimate the experimental results by 40 to 50%, implying that the renormalization of the band width and Fermi velocity from many-body effects is about a factor of 2 or smaller. Considering the electron-phonon coupling constant  $\lambda = 1$  (12), the renormalization is within the range explainable by electron-phonon coupling alone ( $1 + \lambda = 2$ ). Therefore, the expected strong electron-electron correlation in the system (5) does not cause a substantial reduction of the band width, consistent with the density of states extracted from specific heat measurements in bulk  $A_3C_{60}$  [(18) and the discussions in (19)]. Alternatively, the Coulomb interaction on  $C_{60}$  molecules could be suppressed because of the screening effect from the metal substrates in our monolayer samples (20).

From the volume of FS, we can estimate the amount of charge transfer by assuming that the observed experimental dispersion (Fig. 3B) corresponds to two unresolved bands (Fig. 4B). The unoccupied area around a  $\bar{\Gamma}$  point in the 2D FS map (Fig. 2) is about 15 to 40% of the volume of a BZ. Therefore, the charge transfer is  $[1 - (15 \text{ to } 40\%)] \times 2$  (charged subbands)  $\times 2$  (electrons per band)  $\approx 2.9 (\pm 0.5)$  electrons, consistent with 3.3 deduced from the AIPES intensity (Fig. 1E). Although the integral method for determining the charge transfer may have some error (11), this rough analysis sug-

gests that the Luttinger theorem is valid in our electron-doped  $C_{60}$  systems.

The clear observation of electronic band structures and Luttinger Fermi surface in K-doped  $C_{60}$  is remarkable when considering the very short mean-free path estimated in this system (21). The peak width at  $E_F$  extracted from MDC is  $\Delta k = 0.14 \pm 0.02 \text{ \AA}^{-1}$ , yielding a mean-free path  $l = 1/\Delta k = 7.4 \pm 0.9 \text{ \AA}$  here at the experimental temperature, about 25 K. This value is smaller than the nearest-neighbor distance between  $C_{60}$  molecules ( $\sim 10 \text{ \AA}$ ) but larger than the shortest C-C distance between two adjacent molecules ( $\sim 3 \text{ \AA}$ ). It is still unexpected that we can see very clear dispersion and the Luttinger Fermi surface given such a short  $l$ .

Our data show that photoemission data for the  $C_{60}$  family consist of a coherent part near Fermi level and an incoherent part below  $\sim 100$  meV (22). The much larger value of AIPES peak width, 700 to 1200 meV (Fig. 1) (7, 11, 23, 24), is mainly due to many-body effects (25). The coherent band shows dispersing peaks and Fermi surface, and the incoherent features are characterized by a peak at 100 meV and a broad shoulder at about 250 meV (Fig. 1E) (23). The weak 100-meV peak shows very little dispersion (small blue arrows in Fig. 3A and blue circles in Fig. 3C), and its energy position is nearly doping-independent (Fig. 1E, inset). This can be attributed to phonons, as also discussed above with AIPES data. We do know that there are two phonon modes near this energy in the  $C_{60}$  system (3), but the coupling with them would have to be stronger to give rise to a sharper peak than that with other modes. One possibility is that these phonons could yield a special feature in the self-energy, because their frequency is comparable to the bandwidth, which is an unusual situation but typical of fullerenes. In such a case, the spectral weight may be pushed beyond the band edge (26), leading to the formation of the 100-meV peak and/or part of the 250-meV shoulder. This 250-meV shoulder might also be attributed to

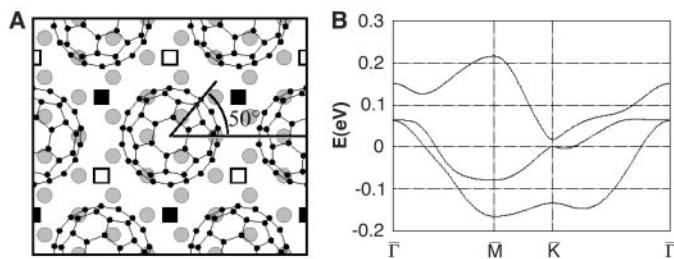
high electron-electron correlation in analogy to the remnant of lower Hubbard band (23).

The data presented here indicate that the  $C_{60}$  system resembles the cuprates or other transition-metal oxides in many ways. In both cases, despite the strong interactions, the effective mass of the "quasi-particle band" is only slightly renormalized, and the velocity of the quasi-particle remains high. In both cases, Fermi surfaces with about the correct Luttinger volume are observed in spite of the extremely short mean-free path, and even the systems have a strong tendency to show inhomogeneity at a very small length scale. This suggests that the Fermi surface and dispersion carry more information on local bonding. It would be very interesting to see whether one can extract more quantitative information by comparing the present data with theoretical calculations such as those using the dynamic mean-field theory (27, 28), which also starts from a local perspective.

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6. ARPES data were collected at the undulator beamline 10.0.1 of the ALS with a linearly polarized synchrotron beam and tunable photon energy and the use of angular mode I of the Scienta 2002 analyzer. AIPES data were collected with the use of the transmission mode. The energy resolution for ARPES experiments reported here is 10 to 15 meV, and the angular resolution for mode I is  $\pm 0.15^\circ$  along the analyzer slit and  $\pm 0.25^\circ$  in the perpendicular direction. (Angular mode II gives a better resolution of  $\pm 0.05^\circ$  along the slit, but mode I was used for this work to get sufficient statistics.) The 127 individual spectra along the  $\sim 13^\circ$  slit could be collected simultaneously. A detailed description is also available in some recent publications, e.g., (29–31). LEED patterns were collected with the use of Er-LEED from Specs (Berlin, Germany).
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**Fig. 4.** Theoretical band dispersion of a  $K_3C_{60}$  monolayer. (A) Atomic configuration of a  $K_3C_{60}$  monolayer that results in the best agreement between the theoretical and the experimental band dispersions. Black dots represent C atoms in the upper half of the molecules, and gray dots represent Ag atoms of the top layer of the Ag(111) surface. A threefold axis of  $C_{60}$  is normal to the surface, and a center of a pentagon close to the axis has an angle of  $50^\circ$  with respect to a nearest-neighbor direction. The center of  $C_{60}$  is 5.6 Å away from the Ag surface. One K atom is located at each open square (3.5 Å away from the Ag surface), and two K atoms are at each solid square (2.9 and 7.6 Å away, respectively). With an angle of  $53^\circ$ , the positions of the C atoms would be the same as those in a (111) layer of solid  $K_3C_{60}$ . (B) Theoretical band dispersion of a  $K_3C_{60}$  monolayer with the orientational configuration of (A). The Fermi level is set to zero in the plot.



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